

ARSENIC IN THERMAL WATERS OF GREECE

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The diffuse occurrence of Arsenic in natural waters, its relevant geochemical mobility in aqueous systems and its toxicity to human beings when consumed in enhanced doses, make this element one of the most problematic challenges of present water research.

Arsenic in groundwater is often associated with geologic sources, but in some locations anthropogenic inputs can be extremely important. Volcanic degassing represents an important natural source of Arsenic to shallow aqueous systems. Arsenic is a minor but recurrent constituent of volcanic gases and geothermal fluids. It is also widely found in epithermal sulphide ore deposits, either as a major constituent (arsenopyrite, orpiment, realgar) or as a minor element in pyrite. As a result of the interaction with deep-rising fluids or leaching of ore deposits, groundwaters circulating in active volcanic-geothermal areas may contain high amounts of Arsenic.

Its presence in groundwater represents one of the major global health issues exposing millions of people to the risk of cancer and other Arsenic-related diseases, especially in southern Asia. Furthermore, previous studies evidenced that widespread areas in northern Greece display Arsenic concentrations above the European Maximum Admissible Concentration (MAC) of 10 µg/l.



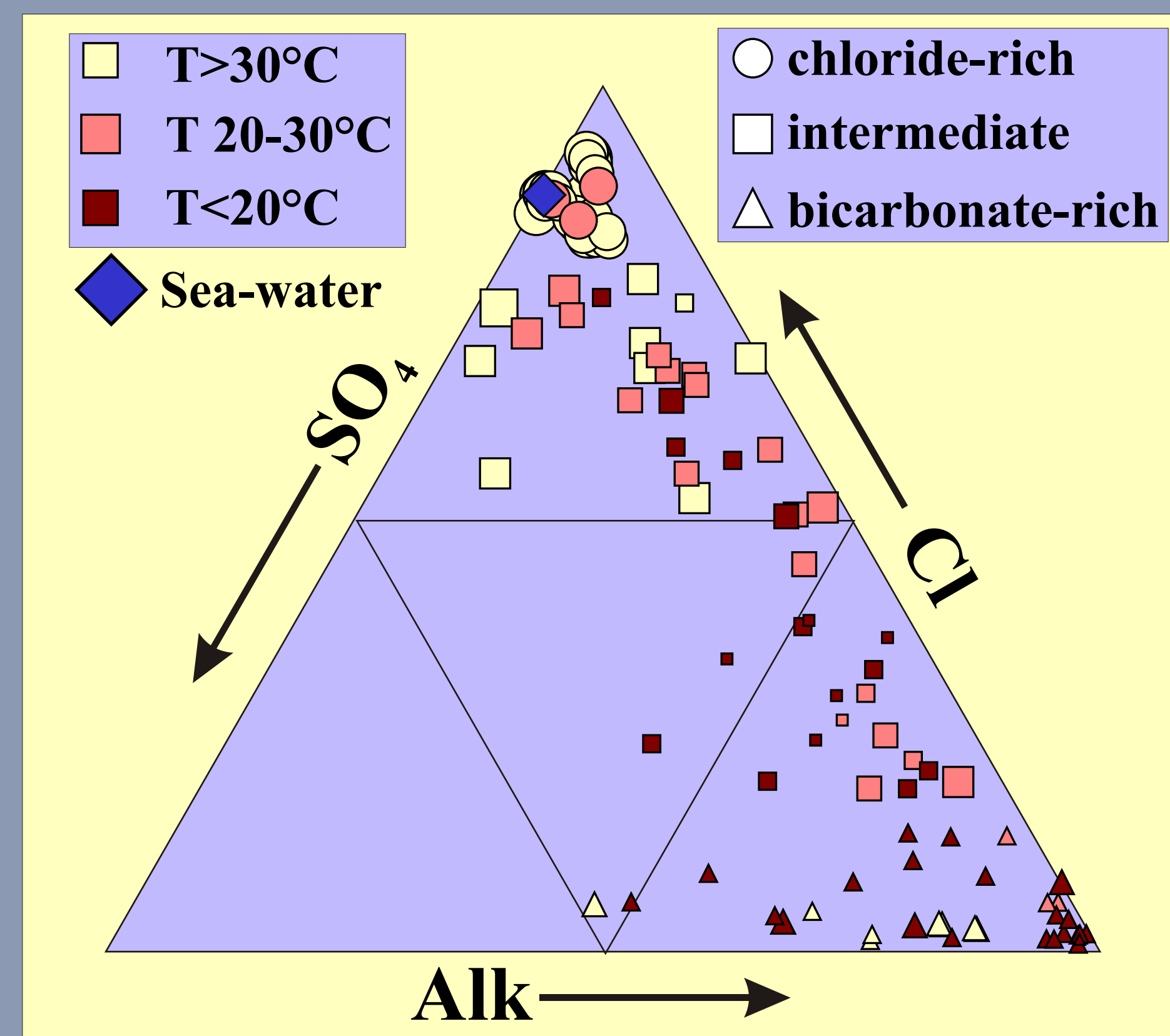
The complex geological history of Greece derives from its position at the contact between the main Eurasian and African plates and the minor Anatolian block. Their relative movements is reflected in the intense geodynamic activity of nearly the whole Hellenic territory.

The most prominent features deriving from this recent (Pliocene-Present) geodynamic activity are the subduction of the African plate along the south Aegean trench and a widespread extensional tectonic. Both phenomena created favorable conditions for the formation of many geothermal systems.

All the volcanic systems (triangles on the left) of the South Aegean active volcanic arc (in orange on the left), in fact, host geothermal fields generally of high enthalpy.

But low to medium enthalpy geothermal systems are also hosted in the hanging walls of several graben systems with their surficial manifestations (thermal springs) emerging along the bordering faults.

Many thermal springs belonging to these geothermal systems have been the target of the present study. The main studied areas are shown as red dots on the left map.



In this study Arsenic concentration were determined in 104 water samples collected in whole Greece. Forty-five of the samples are thermal waters ($T > 30^{\circ}\text{C}$), 24 are hypothermal waters ($T 20-30^{\circ}\text{C}$) and 35 are cold waters ($T < 20^{\circ}\text{C}$). The samples were further subdivided, basing on their major anion contents, in chloride-rich ($\text{Cl} > 80\%$), intermediate ($80\% < \text{Cl} < 15\%$) and bicarbonate-rich ($\text{Cl} < 15\%$). Major anion (left) and major cation (right) composition is shown in the triangular plots. The saline content of the waters is highly variable (TDS range 180 - 41000 mg/l) with the most saline waters (greater symbols in the triangular plots) displaying always chloride-alkaline composition greatly influenced by seawater contamination processes.



Arsenic concentrations span over 4 orders of magnitude ranging from < 0.2 to $5700 \mu\text{g/l}$. They show a fair positive correlation with sampling temperature and cold waters exceed the MAC only in few cases. The inverse relationship with pH emphasizes the importance of water-rock interaction (WRI) processes enhanced by dissolution of acidifying agents of hydrothermal origin such as CO_2 and H_2S , but also probable flocculation and adsorption processes at higher pH values.

This is also reflected in the As-Fe binary diagram where the initial increase of Arsenic with increasing Fe contents reflects the release of both elements to the solution by WRI processes while the lower As values at high Fe contents evidence scavenging processes due to the precipitation of iron-hydroxides.

The contribution of geothermal activity to the Arsenic concentration of the studied groundwaters is further evidenced by the positive correlation between As and thermal-related elements like B and Li.



The samples are too few to highlight a clear geographic distribution and high Arsenic values ($> 100 \mu\text{g/l}$) are found both in continental Greece (Kassandra, Sidirocastro in the north; Thermopyles, Edipsos in the central part; Kaiapha in the Peloponnesus) and along the South Aegean volcanic arc (Methana, Nisyros).

Finally this study confirms the importance of geothermal activity in mobilizing environmentally harmful elements such as Arsenic.

